Surface-Induced Melting of Metal Nanoclusters *

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(Received 5 May 2004)

We investigate the size effect on melting of metal nanoclusters by molecular dynamics simulation and thermodynamic theory based on Kofman's melt model. By the minimization of the free energy of metal nanoclusters with respect to the thickness of the surface liquid layer, it has been found that the nanoclusters of the same metal have the same premelting temperature $T_{\rm pre} = T_0 - T_0(\gamma_{sv} - \gamma_{lv} - \gamma_{sl})/(\rho L\xi)$ (T_0 *is the melting point of bulk metal,* γ_{sv} *the solid–vapour interfacial free energy,* γ_{lv} *the liquid–vapour interfacial free energy,* γ_{sl} *the solid–liquid interfacial free energy,* ρ *the density of metal,* L *the latent heat of bulk metal, and* ξ *the characteristic length of surface-interface interaction) to be independent of the size of nanoclusters, so that the characteristic length* ξ *of a metal can be obtained easily by* $T_{\rm pre}$*, which can be obtained by experiments or molecular dynamics (MD) simulations. The premelting temperature* $T_{\rm pre}$ *of Cu is obtained by MD simulations, then* ξ *is obtained. The melting point* $T_{\rm cm}$ *is further predicted by free energy analysis and is in good agreement with the result of our MD simulations. We also predict the maximum premelting-liquid width of Cu nanoclusters with various sizes and the critical size, below which there is no premelting.*

PACS: 36. 40. Ei, 31. 15. Qg

The melting of nanosized metal clusters has attracted great interest for about one hundred years.[1] Experimentations on deposited[2−5] and free[6,7] metal clusters have found decreasing melting point with decreasing particle size. The linear relation between the depression of melting points ΔT and the curvature $1/R$ of clusters has been derived by macroscopic thermodynamic theory with an approximate form of free energy[1,8−11] and coincides with the simulations[12,13] of the melting of the metal nanoclusters. The improved experimentation for the case of $\Delta\gamma = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} > 0$ shows that there appears to be a surface premelting phenomenon[3] that cannot be explained by the macroscopic thermodynamic theory with the approximate form of free energy. In addition, Shvartsburg *et al.*[14] and Bachele *et al.*[7] experimentally illustrated that the melting point of tin clusters smaller than the crucial radius R_c is higher than that predicted by macroscopic thermodynamic theory with an approximate form of free energy. The abnormal phenomena of melting point are often understood as structure differences[7] or structural transition during heating. Actually, it is difficult to find any relationship between the melting points and the number of atoms for these 'small clusters'.[15]

To understand the premelting phenomenon, Kofman *et al.*[3] introduced an additional free energy term depending on a phenomenological characteristic length ξ to improve the previous approximate form of free energy.[1,8−10] The length indicates the scale of the distance of the two neighbouring interfaces of liquid/vapour and solid/liquid between which there is considerable interaction. Although this model with properly selected value of ξ in fact provided a significant improvement compared to previous thermodynamic theoretical approaches, Kofman *et al.* did not discuss how to obtain the proper value of ξ. Obviously, a general way to decide the phenomenological characteristic length ξ, either for the view of the completeness of the model or for convenience of applications, is of great importance.

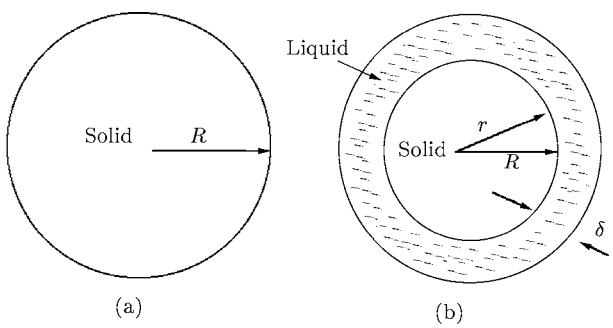

Fig. 1. Two configurations: solid particle (a) and solid clusters with a surface melted layer (b).

In this Letter, we give a simple universal relation between the parameter ξ and premelting temperature $T_{\rm pre}$ by analysis of Kofman's free energy expression. This relation is independent of the size of nanoclusters, and is used to calculate the value of ξ from $T_{\rm pre}$, which can be obtained by experiments or molecular dynamics simulations. To validate our method, we achieve the premelting point $T_{\rm pre}$ of Cu by MD simulation, and obtain ξ, and then compare the melting

* Supported by the National Natural Science Foundation of China under Grant No 10172088, and the Knowledge Innovation Programme of Chinese Academy of Sciences (No KJCX2-SW-L2).

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points given by our simulations with those calculated by using the free energy. Some other melting properties of Cu nanoclusters are also presented. Of course, another significance of our work is to verify the validity of Kofman's phenomenological melt model as shown in Fig. 1.

We now consider the thermodynamic analysis for the melting of metal clusters with Kofman's melt model. Neglecting the difference of the densities of solid and liquid, the free energy of nanoclusters wetted with thickness of δ is[3]

$$\begin{aligned} F =& \frac{4}{3}\pi r^3 \rho f_s + 4\pi r^2 \gamma_{sl} \\ &+ \frac{4}{3}\pi (R^3 - r^3)\rho f_l + 4\pi R^2 \gamma_{lv} + F', \\ r =& R - \delta, \\ F' =& 4\pi (R^2 \gamma_{sv} - R^2 \gamma_{lv} - r^2 \gamma_{sl}) e^{-\delta/\xi}, \end{aligned} \tag{1}$$

where ρ is the number density of atoms, f_s is the free energy of the atom in solid phase, f_l is the free energy of the atom in liquid phase, γ_{sv} is the interfacial free energy of solid/vapour, γ_{lv} is the interfacial free energy of liquid/vapour, and γ_{sl} is the interfacial free energy of solid/liquid.

With $\delta_c = R - 2\gamma_{sl}/[\rho(f_l - f_s)]$, Eq. (1) can be rewritten as

$$\begin{aligned} \frac{F - F_0}{4\pi R^2 \gamma_{sl}} =& (1 - \delta/R)^2 \left(1 - \frac{2}{3}\frac{(1 - \delta/R)}{(1 - \delta_c/R)}\right) \\ &+ \frac{\gamma_{sv} - (\gamma_{lv} + (1 - \delta/R)^2 \gamma_{sl})}{\gamma_{sl}} e^{-(\delta/R)(R/\xi)}, \end{aligned} \tag{2}$$

with

$$F_0 = 4\pi R^2 \gamma_{lv} + (4/3)\pi R^3 \rho f_l.$$

The first-order partial derivative of free energy (1) reads

$$\begin{aligned} \frac{\partial (F/(8\pi\gamma_{sl}R^2))}{\partial(\delta/R)} =& (1 - \delta/R)\frac{(\delta_c/R - \delta/R)}{(1 - \delta_c/R)} \\ &+ \frac{\gamma_{sv} - (\gamma_{lv} + (1 - \delta/R)^2 \gamma_{sl})}{2\gamma_{sl}} \\ &\cdot e^{-(\delta/R)(R/\xi)}(-R/\xi) \\ &+ (1 - \delta/R) e^{-(\delta/R)(R/\xi)}. \end{aligned} \tag{3}$$

By using $(f_l - f_s) = L(T_0 - T)/T_0$[16] with T_0 being the melting point of bulk metal and L being the latent heat of bulk metal, the minimization of free energy (Eq. (1)) presents the relation between the thickness of premelting layer and the temperature,[3] i.e.

$$\begin{aligned} \frac{T_0 - T}{T_0} =& \frac{2\gamma_{sl}}{\rho L r}(1 - e^{-\delta/\xi}) \\ &+ \frac{(\gamma_{sv} - \gamma_{lv} - \gamma_{sl} r^2/R^2)R^2}{\rho L \xi r^2} e^{-\delta/\xi}. \end{aligned} \tag{4}$$

Using the condition that $T_{\rm pre}$ is the temperature corresponding to $\delta = 0$ in Eq. (4), we obtain

$$T_{\rm pre} = T_0 - \frac{T_0(\gamma_{sv} - \gamma_{lv} - \gamma_{sl})}{\rho L \xi}. \tag{5}$$

Equation (5) indicates that the premelting temperatures of nanoclusters do not change with their sizes.

In MD simulations, the potential function is important to obtain physical properties of materials.[17] For the simulations of Cu nanoclusters, we use the Finnis–Sinclair (FS) potential,[18,19] with the parameters determined by the fitting to the sublimation energy, equilibrium lattice constant, elastic constants, and vacancy-formation energies of the pure metals.[20] The extended-system (NPT), in which the systems are coupled to a bath with constant temperature and constant pressure, is used with zero pressure.[21] The Verlet velocity scheme is implemented as a time integration algorithm.[22] After equilibration at 300 K for 30 ps with time steps of 2.5 fs, the clusters were taken from low temperature to 2000 K in steps of 20 K through 15 ps relaxation time for each temperature, and the temperature steps reduce to 5 K with the same heating rate near the melting points. The premelting temperature of Cu nanoclusters is obtained with the Honeycutt–Anderson pair analysis technique.[23] The number of the 1421 bond pairs, which characterize the *fcc* structure, reduces slowly during heating when the nanocluster is in solid phase, while it decreases in a large scale during premelting. The number of the bond pairs 1421 in Nc1205 (a nanocluster including 1205 atoms) at different temperatures is shown in Fig. 2, from which we achieve $T_{\rm pre}$ of this nanocluster to be 900 K, where the number of the pairs 1421 decreases abruptly.

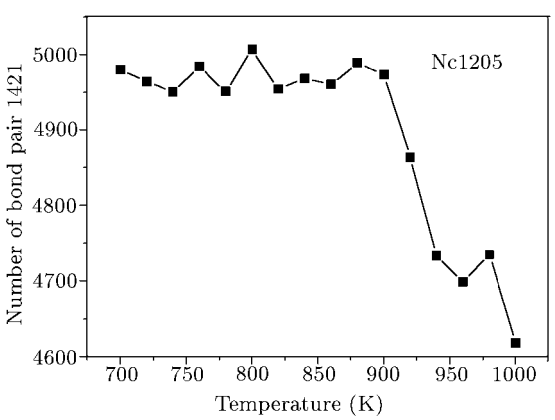

Fig. 2. The number of bond pairs 1421 in Nc1205 at different temperatures by molecular dynamics simulation.

Similarly, we achieve the premelting temperatures of nanoclusters including 791–12839 atoms to be between 880 K and 920 K. However, the smaller nanoclusters of Nc531 and Nc321 present the lower premelting temperatures of 740 K and 680 K, respectively,

which may be due to the fact that the nanoclusters possess too few atoms to be described by the continuous model or macro-thermodynamics, so that in the scope of thermodynamics, the data of smaller clusters Nc531 and Nc321 should be omitted. Thus, we estimate the $T_{\rm pre}$ of Cu nanoclusters to be 900 K, the average of 880 K and 920 K. Considering the approximation contained in Kofman's model, such as the constant density ρ, the error 20 K is acceptable. Equation (5) and the known $T_{\rm pre}$ gives $\xi = 0.031$ nm (data: $\gamma_{sv} = 1592\,{\rm mJ/m^2}$, $\gamma_{lv} = 1310\,{\rm mJ/m^2}$, $\gamma_{sl} = 263\,{\rm mJ/m^2}$,[24] $T_0 = 1356$ K, $L = 13.02$ kJ/mol, and $\rho = 8960\,{\rm kg/m^3}$).

Using MD simulations with the criterion of maximum heat capacity,[12] we determine the melting temperatures $T_{\rm cm}$ of Cu nanoclusters including different atom numbers and compare with those predicted by the free energy analysis. The heating rate selected is small enough to ensure that the $T_{\rm cm}$ obtained is close to that in the thermodynamic equilibrium.

To illustrate the calculation of the melting temperatures $T_{\rm cm}$ of Cu nanoclusters, we give the free energy and its first order derivative of Cu nanocluster with radius $R = 8.0A_0$ (A_0 is the lattice constant of Cu) as a function of δ/R by Eqs. (2) and (3), as shown in Figs. 3 and 4 respectively.

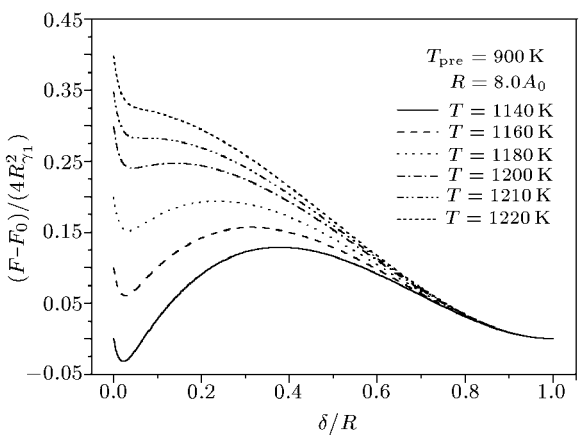

Fig. 3. Free energy of Cu nanocluster as a function of surface liquid width δ at several temperatures.

Figure 4 shows the first order derivative of free energy of Cu nanocluster as a function of surface liquid width δ at different temperatures in the range 1140–1220 K. With increasing temperature, the peak value of the derivative of free energy decreases from positive to negative. For the temperatures $T \geq 1210$ K, $\partial[F/(8\pi\gamma_{sl}R^2)]/(\partial(\delta/R) \leq 0$ is satisfied for all δ/R, which means that the free energy decreases continuously until the cluster melts completely (as shown in Fig. 3 for $T \geq 1210$ K), therefore 1210 K is the melting point $T_{\rm cm}$ of Cu nanocluster with radius size of $8.0A_0$. $T_{\rm cm}$ of Cu nanoclusters with arbitrary sizes can also be obtained in the same way.

The predicted melting points of Cu nanoclusters shown in Fig. 5 are in good agreement with those achieved by our MD simulations for clusters of 531 to 12839 atoms. The larger departure of the simulated melting point of Nc321 from the theoretical cure results from the small number of the atoms, which is mentioned above for the departure of $T_{\rm pre}$ from that of other larger clusters. Thus, the thermodynamic theory is suitable for nanoclusters with atoms more than about 500.

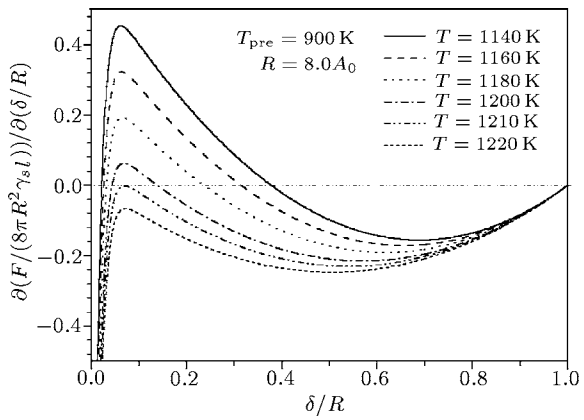

Fig. 4. The first order derivative of free energy of Cu nanocluster as a function of surface liquid width δ at different temperatures.

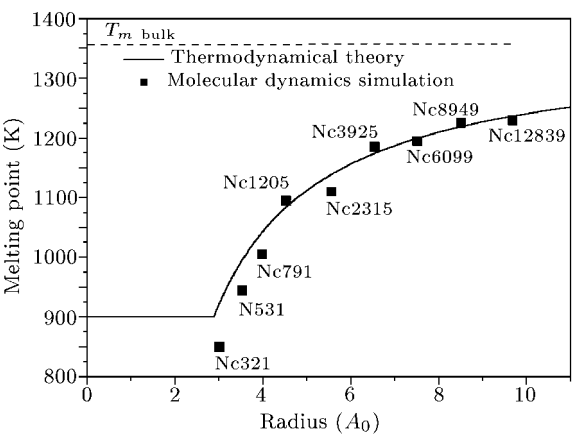

Fig. 5. Melting points of clusters by thermodynamics theory and MD simulations.

Some other melting behaviour of Cu nanoclusters can also be predicted by the free energy curves shown in Figs. 3 and 4. In Fig. 4, the curve at temperature $T_{\rm cm} = 1210$ K is tangent with the zero line at the point indicating the maximum coexistent liquid width $\delta_{\rm Max}$. Any curve with temperature below $T_{\rm cm}$ has three intersections with the zero line. The smallest one corresponds to the wave valley in Fig. 3 and gives the thickness of premelting liquid layer, which increases with increasing temperature. For the cure at temperature above $T_{\rm cm}$, the sole intersection point at $\delta/R = 1$ indicates the whole cluster being liquid.

In Fig. 6, the maximum liquid width increases with increasing size of Cu nanoclusters and ranges from $0.41A_0$ ($R = 2.88A_0$) to $0.83A_0$ ($R = 50A_0$). Cu nanoclusters with radius less than R_c ($2.87A_0$) do not premelt and will melt completely at $T_{\rm pre}$. This phenomenon can be interpreted by the monotonic decrease of the free energy of those clusters at $T_{\rm pre}$ with liquid width, as shown in Fig. 7.

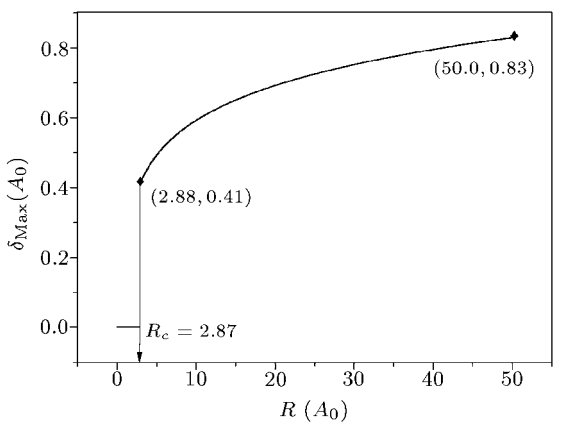

Fig. 6. Maximum liquid width of Cu nanoclusters before melting.

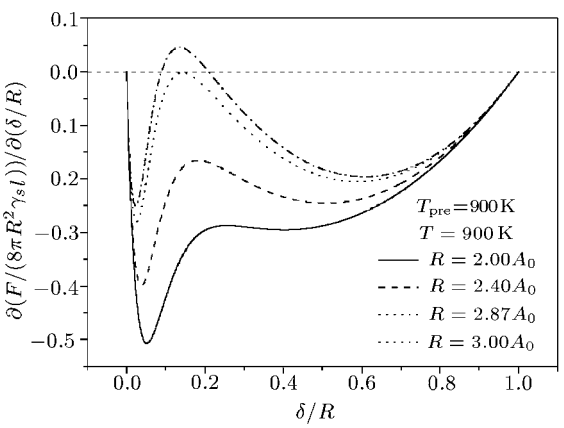

Fig. 7. The first order derivative of free energy of Cu nanoclusters in radius near R_c.

In summary, we have studied the melting properties of metal nanoclusters in terms of Kofman's model combined with MD simulation. A simple general relation between the characteristic length ξ of a metal and its premelting temperature $T_{\rm pre}$ is obtained to be $T_{\rm pre} = T_0 - T_0(\gamma_{sv} - \gamma_{lv} - \gamma_{sl})/(\rho L\xi)$, which shows that $T_{\rm pre}$ is independent of sizes of nanoclusters and can be used to achieve the value of ξ, by which we can predict the melting properties of the metal clusters through the expression of the free energy. The melting points of Cu nanoclusters predicted in this way are in good agreement with those obtained by our MD simulation, which validates our method. Our study illustrates that thermodynamic interpretation of the melting of Cu nanoclusters is valid only for atom number more than about 500, which was also given by Yue Qi *et al.* for Ni.[12] Some other melting properties of Cu nanoclusters are also presented. For example, there is a critical size R_c ($2.87A_0$), below which no premelting phenomenon appears. For Cu nanoclusters with radii less than $50A_0$, the maximum liquid width of Cu nanoclusters increases with the increasing radius and is smaller than $0.83A_0$.

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